

Supporting Information

One-pot self-assembled AgNW aerogel electrode with ultra-high electric conductivity for intrinsically 500% super-stretchable high-performance Zn-Ag battery

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Experimental Section

Materials and instrumentation. All chemicals and solvents were purchased from Sigma-Aldrich (Shanghai, CN), Alfa, Aladdin Biochemical Technology Co., Ltd (Shanghai) and used as received. A Hitachi SU8010 field emission SEM and a FEI Tecnai G2 F30 TEM were utilized to take microscopic images and diffraction patterns. XRD was conducted through a Rigaku D/max-2500, which was recorded from 20-85° with a step size of 0.1° at 1.5 seconds per step. XPS and DSC-TGA thermal analyses were performed with a PHI 5000 Versa Probe II and Netzsch STA 449 F3, respectively. FT-IR was carried out by a Nicolet-380.

Synthesis of AgNW aerogel. For a typical synthesis, 48 ml of ethylene glycol (EG, solvent and reductant) containing AgNO₃ (60 mM) and PVP (MW = 360 K, 0.03 mM) was added in a PTFE reactor and pre-heated at 50 °C for 10 mins to initiate the crystallization of AgCl seeds. Subsequently, 12 ml of surface-activated cellulose and FeCl₃ (0.16 mM) in EG was added to the reactor and vigorously stirred for 5 mins to attain a homogeneous state. After stirring, the solution was heated at 180 °C for another 2 hours and cooled down in the air to room temperature, when a white jelly-like alcogel with a three-dimensional porous structure of highly crosslinked AgNW was obtained. The as-made AgNW alcogel was immersed in deionized water with a flowing speed of 10 mL/min. After 6 hours of rinsing, the residual reactants including EG, AgNO₃, PVP and FeCl₃ were fully dissolved and removed together with the free AgNW monomers and nanoparticles. Then, the cleaned AgNW alcogel was performed solvent replacement by ethanol with a flowing speed at 5 mL/min. Within 4 hours, a purified AgNW alcogel containing only ethanol could be obtained. Following the cleaning, the AgNW alcogel was dried by CO₂ supercritical fluid at 35 °C and 8 MPa for 1 hour, after which the AgNW aerogel was finally obtained.

Synthesis of PANa hydrogel electrolyte. 48 g acrylic acid [1] monomers were first added into 54 g deionized water, while 26.7 g sodium hydroxide was dissolved in 18 g deionized water. After intensive stirring in an ice bath environment, the sodium

hydroxide solution was slowly dropped into the AA solution until the mixed solution was close to neutral. Then, 0.78 g ammonium persulfate (APS) was added into the mixed solution and stirred for 20 minutes before being placed in a 40 ± 2 °C environment to polymerize. Finally, the PANA electrolyte was produced after the as-synthesized hydrogel was fully dried at 100 °C and soaked in a concentrated solution (100 mL) of 10 M sodium hydroxide for 48 h.

Fabrication and electrochemical characterization of the Zn-Ag battery. Zinc spring of 10 cm length was first cleaned by anhydrous ethanol and deionized water. Next, the AgNW aerogel was compressed into a planar film of 1 cm width and 7 cm length and directly mounted on carbon nanotube paper (mass loading around 4-7.5 mg/cm²) to enhance mechanical strength. Then, the Zn-Ag battery was assembled by paving the AgNW aerogel on pre-stretched PANa hydrogel electrolyte directly and releasing on the Zn spring.

CV and GCD were tested through a CHI 760E potentiostat. The capacity was calculated according to the equation: $C=It/3600$, where I is the discharge current density (mA cm⁻²) and t is the discharge time (s). Then, the energy density was calculated through the integration of the discharge curve: $E=I\int U(t)dt/3600$, where U(t) is the voltage during discharge.

Electrical measurement. The electrical measurement was carried out using a four-probe test unit. Sheet resistances of AgNW aerogel and PANa hydrogel electrolyte were measured at multiple sites to obtain an average value. The resistivity (ρ) was calculated by $\rho=k\times R_a\times thickness$, where k is the shape correction factor (4.455), R_a is the measured resistance value. The conductivity was calculated by $\sigma=1/\rho$.

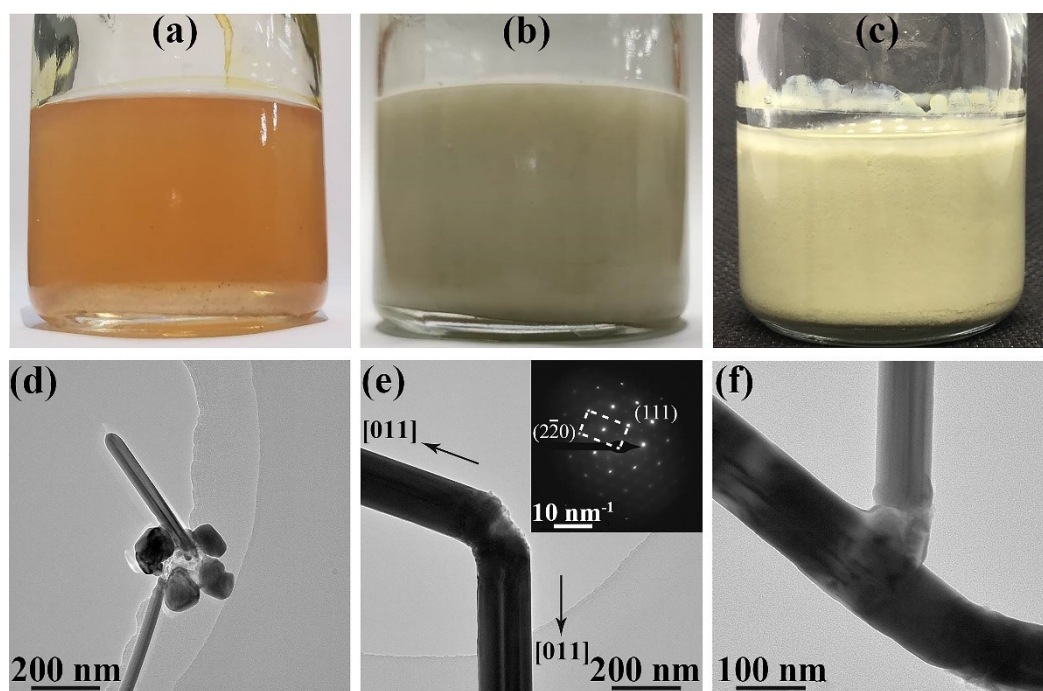


Figure S1. Synthesis process of the aerogel with highly crosslinked AgNW. (a-c) Optical images of the reaction solution with AgCl seeds after stirring, nucleation of Ag clusters and growth of AgNW. (d-e) TEM images illustrate the multi-directional growth of AgNW from AgCl seeds and the formation of AgNW with broken-line or branched structures.

The original reaction solution containing AgCl seeds and FeCl₃ showed dark yellow after stirring. Once the reaction was initiated by heating, the solution granularly turned grey due to the consumption of FeCl₃ and the formation of Ag clusters on AgCl seeds. These clusters further grew to AgNW. Finally, the developed AgNW intertwined, interconnected and formed a macroscopic three-dimensional structure with the progress of the reaction, leading to a unique white jelly-like appearance different from initial nanomaterials in the solution.

The multi-directional growth of AgNW from AgCl@Ag clusters was evident according to the TEM image (Fig. S1d). These clusters decomposed and shrank as AgNW grew, finally transforming to the joint structure in Fig. S1e-f.

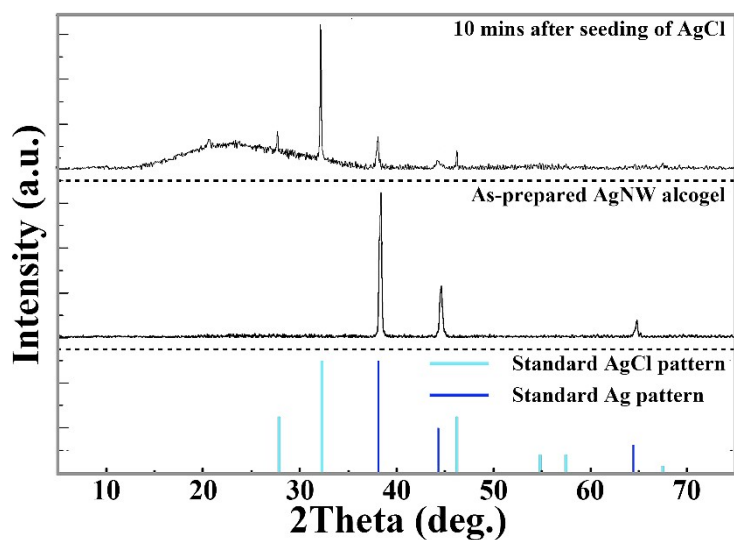


Figure S2. XRD pattern of the seeds obtained from the reacting solution and aerogel, from which the presence and decomposition of AgCl can be confirmed.

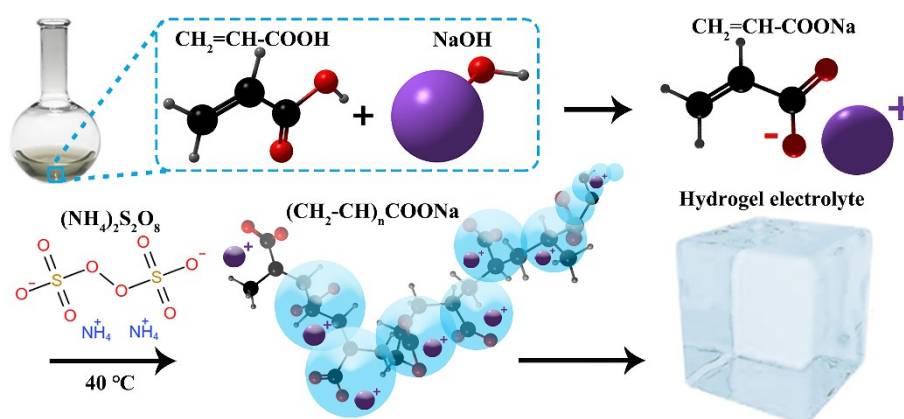


Figure S3. Schematic illustration of synthesis of PANa hydrogel electrolyte.

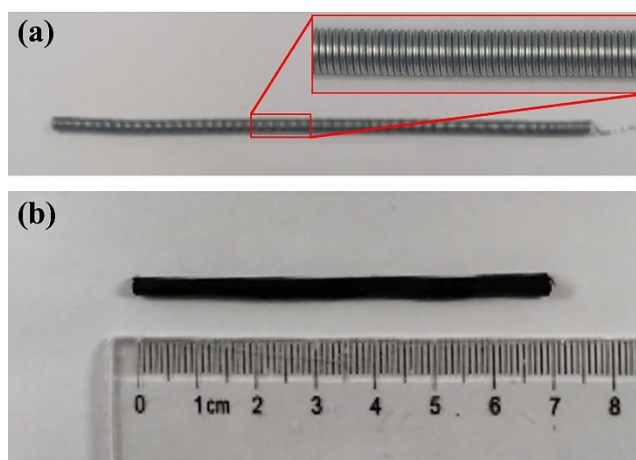


Figure S4. Optical photos of (a) Zn spring, and (b) the as-fabricated intrinsically superstretchable Zn-Ag battery.

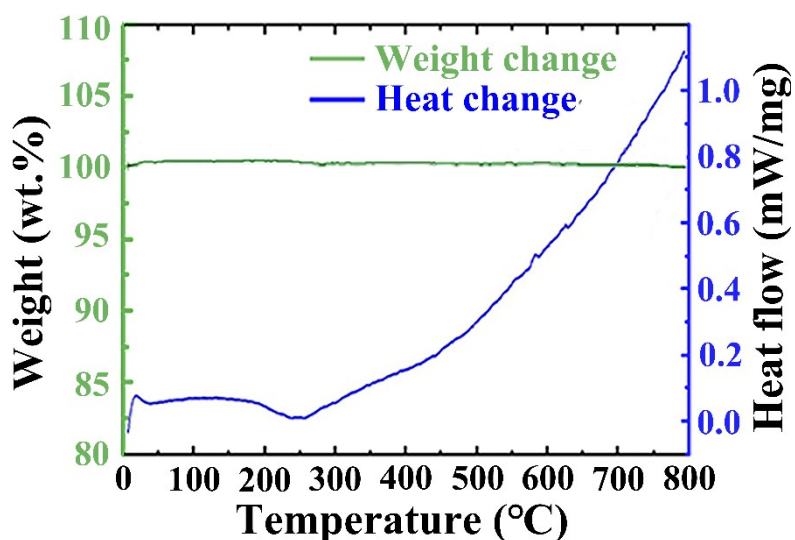


Figure S5. DSC-TGA profiles of as-fabricated AgNW aerogel.

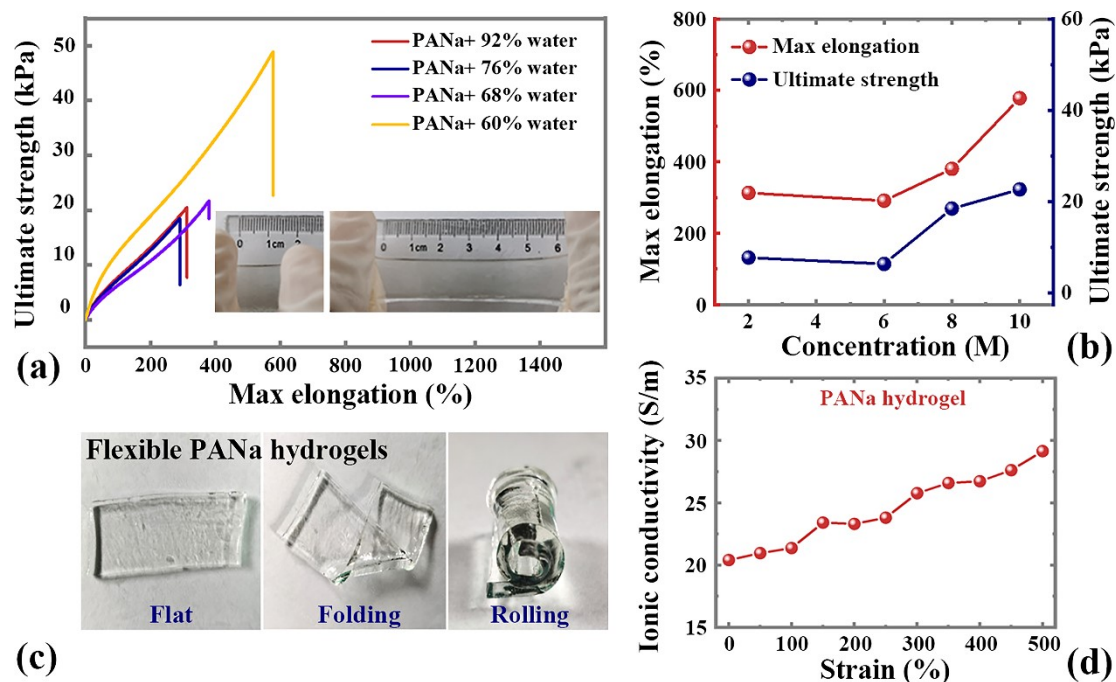


Figure S6. Characteristics of the PANA hydrogel electrolyte. (a) Ultimate strength versus maximum elongation of the synthesized PANA hydrogel electrolyte containing different water concentrations. Insets are photos of the as-synthesized and 500% stretched hydrogel. (b) Ultimate strength and maximum elongation of PANA hydrogel electrolyte containing different NaOH concentrations. (c) The PANA hydrogel under various mechanical deformations. (d) The ionic conductivity of PANA hydrogel electrolyte at different strains.

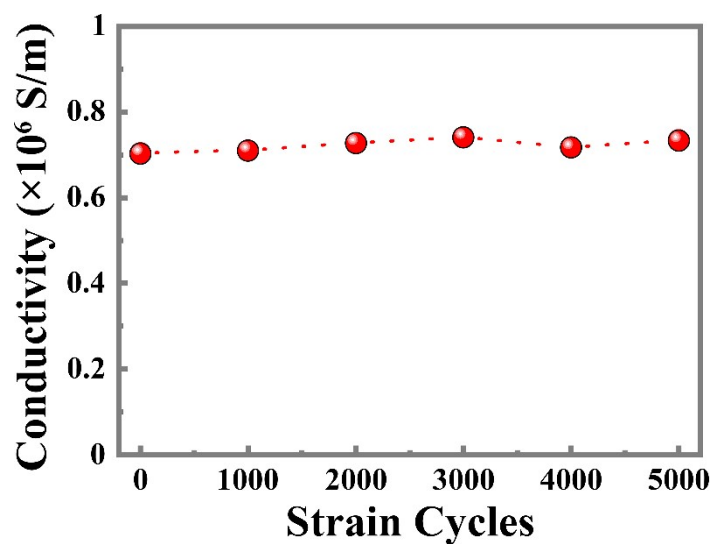


Figure S7. The electronic conductivity of the as-fabricated AAF electrode stuck on the surface of pre-stretched PANa hydrogel electrolyte in 5000 cycles of 500% stretching.

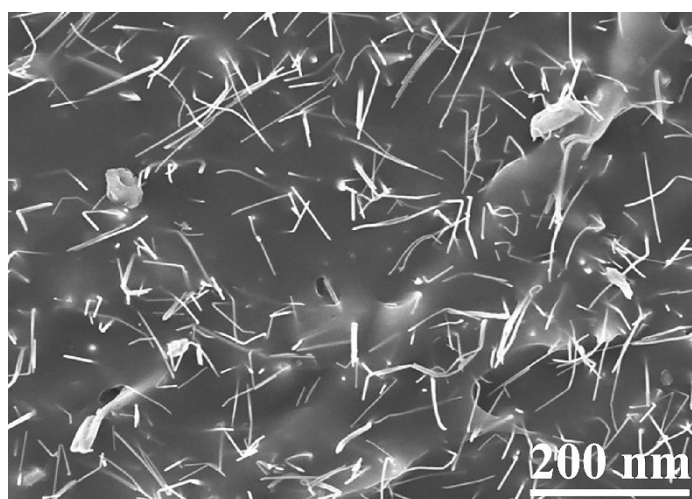


Figure S8. Morphology of AgNWs from AAF that penetrated and intertwined with PANa hydrogel electrolyte.

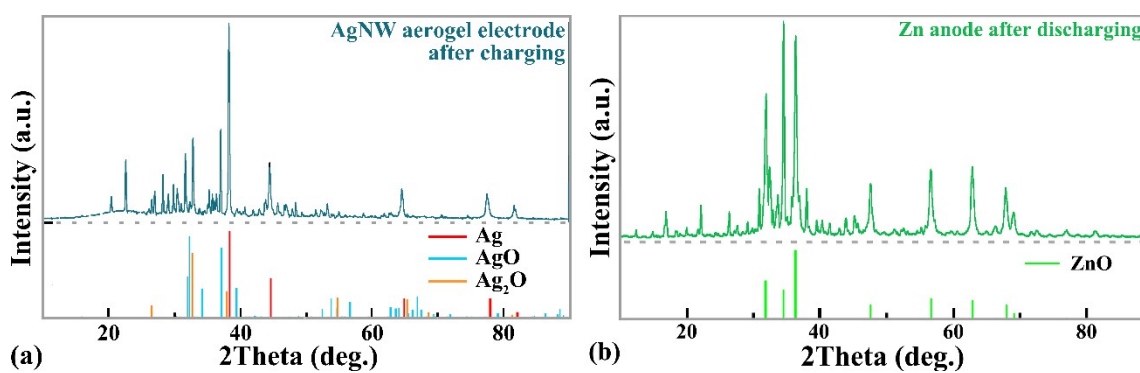


Figure S9. XRD patterns of AgNW and Zn electrodes after charging and discharging.

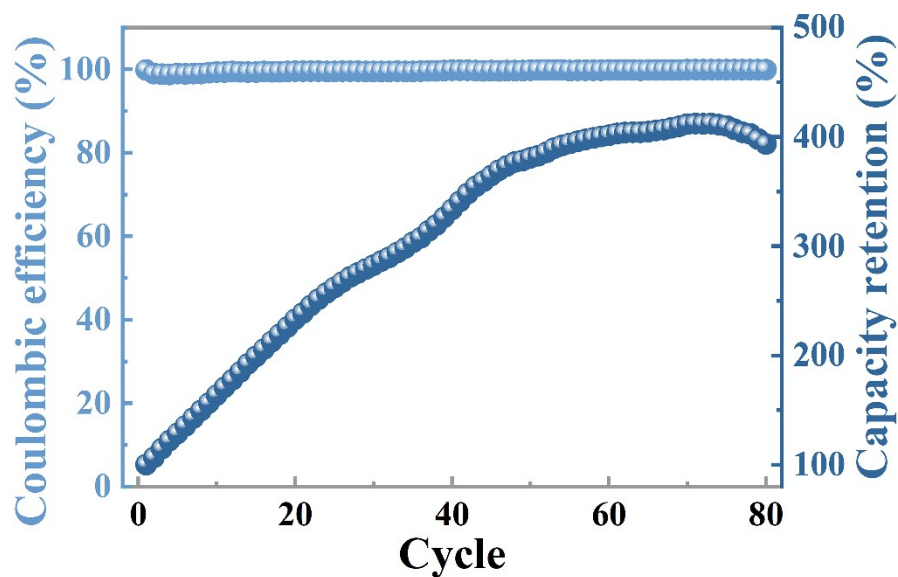


Figure S10. Cycling performance of the intrinsically super-stretchable Zn-Ag battery, where the Coulombic efficiency remained over 98.7% and the capacity increased due to the activation of the AgNW aerogel on PANA hydrogel electrolyte.

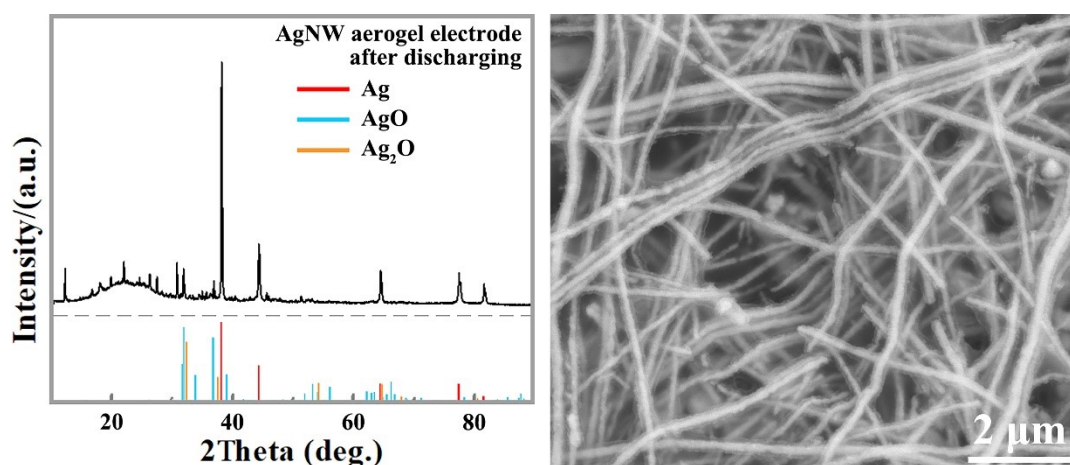


Figure S11. XRD patterns and the related SEM morphology of AgNW aerogel electrodes after cyclic test.

Reference:

1. Braam, K. and V. Subramanian, *Advanced Materials*, 2015. **27**, 689-694.